Benzofurans or Isochromenes via the Ring-Opening Cyclization of Cyclopropene Derivatives with Organolithiums

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General

All common reagents were obtained from commercial suppliers and used without further purification. CH₂Cl₂ was distilled from K₂CO₃ before use. THF was distilled from Na/benzophenone.

Starting Materials:

General procedure for the protection of the hydroxyl groups.

(1) 2-Iodophenyl acetate 7a

To a dried flask were added 2-iodophenol (11.06 g, 50.3 mmol) and 100 mL of CH₂Cl₂. Then a solution of DMAP (0.32 g, 2.6 mmol) and Et₃N (7.60 g, 75.2 mmol) in 50 mL of CH₂Cl₂ was added. The resulting mixture was stirred at room temperature, and a solution of Ac₂O (6.14 g, 60.1 mmol) in 50 mL of CH₂Cl₂ was added dropwise via an addition funnel. After complete conversion of the starting materials as monitored by TLC, 100 mL of water was added, the organic layer was separated. The aqueous phase was extracted with CH₂Cl₂ (50 mL × 3), the organic phase was combined and washed with a saturated aqueous solution of NaCl, and dried over anhydrous Na₂SO₄. The solvent was evaporated. Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded 7a² (12.84 g, 97 %): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.83 (dd, J = 7.8 Hz, 1.5 Hz, 1 H), 7.41-7.33 (m, 1 H), 7.10 (dd, J = 8.0 Hz, 1.4 Hz, 1 H), 6.98 (td, J = 7.7 Hz, 1.5 Hz, 1 H), 2.37 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.1, 150.8, 138.9, 129.1,
127.3, 122.8, 90.4, 20.9; MS (EI, m/z) 262 (M⁺, 80.98), 220 (100); IR (neat, cm⁻¹) 3064, 1768, 1464, 1439, 1367, 1182, 1117, 1043, 1017.

(2) 2-Iodo-4-methylphenyl acetate 7b

\[
\begin{align*}
&\text{Me} & & | & & \text{I} \\
&\text{OH} & & \text{Ac}_2\text{O} & & \text{Et}_3\text{N} (1.5 \text{ equiv.}) & & \text{CH}_2\text{Cl}_2, \text{rt}, 11 \text{ h} \\
&\text{Me} & & | & & \text{I} \\
&\text{OAc} & & & & & & 7b (86 \%)
\end{align*}
\]

The reaction of 2-iodo-4-methylphenol (8.09 g, 34.6 mmol), Ac₂O (4.15 g, 40.7 mmol), DMAP (0.21 g, 1.7 mmol), Et₃N (5.13 g, 50.8 mmol) and 100 mL of CH₂Cl₂ afforded 7b (8.18 g, 86 %): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.61 (s, 1 H), 7.10 (d, J = 8.4 Hz, 1 H), 6.94 (d, J = 8.4 Hz, 1 H), 2.31 (s, 3 H), 2.26 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.5, 148.8, 139.4, 137.4, 129.9, 122.3, 90.1, 21.0, 20.2; MS (EI, m/z) 276 (M⁺, 9.66), 43 (100); IR (neat, cm⁻¹) 2923, 1765, 1593, 1480, 1430, 1367, 1213, 1183, 1038, 1009.

(3) 2-Iodo-5-methylphenyl acetate 7c

\[
\begin{align*}
&\text{Me} & & | & & \text{I} \\
&\text{OH} & & \text{Ac}_2\text{O} & & \text{Et}_3\text{N} (1.5 \text{ equiv.}) & & \text{CH}_2\text{Cl}_2, \text{rt}, 9 \text{ h} \\
&\text{Me} & & | & & \text{I} \\
&\text{OAc} & & & & & & 7c (96 \%)
\end{align*}
\]

The reaction of 2-iodo-5-methylphenol (2.28 g, 9.7 mmol), Ac₂O (1.15 g, 11.3 mmol), DMAP (57.9 mg, 0.47 mmol), Et₃N (1.42 g, 14.1 mmol) and 40 mL of CH₂Cl₂ afforded 7c (2.58 g, 96 %): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.55 (d, J = 8.1 Hz, 1 H), 6.81 (s, 1 H), 6.68 (d, J = 8.1 Hz, 1 H), 2.24 (s, 3 H), 2.20 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.5, 150.8, 139.8, 138.6, 128.5, 123.5, 86.1, 21.1, 20.8; MS (EI, m/z) 276 (M⁺, 20.11), 234 (100); IR (neat, cm⁻¹) 2922, 1772, 1475, 1368, 1195, 1155, 1019; HRMS Calcd for C₉H₆O₂I (M⁺): 275.9647; Found: 275.9646.
(4) 4-Chloro-2-iodophenyl acetate 7d

\[
\begin{align*}
\text{Cl} & \quad \text{I} \\
\text{OH} & \quad + \quad \text{Ac}_2\text{O} \\
\text{1.1 equiv.} & \quad \text{5 mol\% DMAP} \\
\text{Et}_3\text{N (1.5 equiv.)} & \quad \text{CH}_2\text{Cl}_2, \text{rt}, 11\text{h} \\
\text{Cl} & \quad \text{I} \\
\text{OAc} & \quad \text{7d (88 \%)}
\end{align*}
\]

The reaction of 4-chloro-2-iodophenol (5.11 g, 20.1 mmol), Ac₂O (2.47 g, 24.2 mmol), DMAP (0.14 g, 1.1 mmol), Et₃N (3.23 g, 32.0 mmol) and 80 mL of CH₂Cl₂ afforded 7d \(^2\) (5.23 g, 88 %): Solid; mp 56-57 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl₃) \(\delta\) 7.81 (d, \(J = 2.4\) Hz, 1 H), 7.33 (dd, \(J = 8.7\) Hz, 2.4 Hz, 1 H), 7.02 (d, \(J = 8.4\) Hz, 1 H), 2.36 (s, 3 H); \(^1^3\)C NMR (CDCl₃, 75 MHz) \(\delta\) 168.5, 150.0, 138.7, 132.2, 129.6, 123.7, 91.0, 21.2; MS (EI, m/z) 298 (M⁺\(^{37}\)Cl, 1.54), 296 (M⁺\(^{35}\)Cl, 4.68), 43 (100); IR (KBr, cm\(^{-1}\)) 3094, 1748, 1573, 1463, 1367, 1213, 1189, 1096, 1035, 1009.

(5) 5-Chloro-2-iodophenyl acetate 7e

\[
\begin{align*}
\text{Cl} & \quad \text{I} \\
\text{OH} & \quad + \quad \text{Ac}_2\text{O} \\
\text{1.2 equiv.} & \quad \text{5 mol\% DMAP} \\
\text{Et}_3\text{N (1.5 equiv.)} & \quad \text{CH}_2\text{Cl}_2, \text{rt}, 10\text{h} \\
\text{Cl} & \quad \text{I} \\
\text{OAc} & \quad \text{7e (93 \%)}
\end{align*}
\]

The reaction of 5-chloro-2-iodophenol (2.21 g, 8.7 mmol), Ac₂O (1.07 g, 10.5 mmol), DMAP (54.2 mg, 0.44 mmol), Et₃N (1.32 g, 13.1 mmol) and 40 mL of CH₂Cl₂ afforded 7e (2.40 g, 93 %): Solid; mp 48-49 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl₃) \(\delta\) 7.65 (d, \(J = 8.4\) Hz, 1 H), 7.05 (s, 1 H), 6.90 (d, \(J = 8.7\) Hz, 1 H), 2.28 (s, 3 H). \(^1^3\)C NMR (CDCl₃, 75 MHz) \(\delta\) 168.1, 151.7, 139.7, 135.0, 127.9, 123.6, 88.0, 21.1; MS (EI, m/z) 298 (M⁺\(^{37}\)Cl, 5.85), 296 (M⁺\(^{35}\)Cl, 16.75), 254 (100); IR (KBr, cm\(^{-1}\)) 3027, 2939, 1758, 1567, 1459, 1367, 1213, 1189, 1088, 1018; Elemental analysis Caled for C₈H₆ClIO₂: C, 32.41; H, 2.04; Found: C, 32.43; H, 2.05.
(6) 5-Fluoro-2-iodophenyl acetate 7f

\[
\begin{align*}
\text{F} & \quad \text{OH} + \quad \text{Ac}_2\text{O} \\
1.2 \text{ equiv.} & \quad \text{5 mol\% DMAP} \\
\text{CH}_2\text{Cl}_2, \text{rt}, 8 \text{ h} & \quad \text{Et}_3\text{N (1.5 equiv.)} \\
\end{align*}
\]

7f (93 %)

The reaction of 5-fluoro-2-iodophenol (4.74 g, 19.9 mmol), Ac₂O (2.45 g, 24.0 mmol), DMAP (0.12 g, 1.0 mmol), Et₃N (3.04 g, 30.1 mmol) and 80 mL of CH₂Cl₂ afforded 7f (5.20 g, 93 %): Liquid; ^1H NMR (300 MHz, CDCl₃) δ 7.74 (dd, J = 8.6 Hz, 6.2 Hz, 1 H), 6.89 (dd, J = 9.0 Hz, 2.7 Hz, 1 H), 6.76 (td, J = 8.4 Hz, 2.4 Hz, 1 H), 2.34 (s, 3 H). ^13C NMR (CDCl₃, 75 MHz) δ 168.0, 162.9 (d, J = 247.5 Hz), 151.8 (d, J = 11.3 Hz), 139.5 (d, J = 9.0 Hz), 115.0 (d, J = 21.8 Hz), 111.2 (d, J = 24.8 Hz), 83.8 (d, J = 3.8 Hz), 21.0; ^19F NMR (282 MHz, CDCl₃) δ -111.1; MS (EI, m/z) 280 (M⁺, 15.46), 132 (100); IR (neat, cm⁻¹) 3089, 1776, 1589, 1472, 1408, 1369, 1272, 1197, 1146, 1107, 1018; HRMS Calcd for C₈H₆O₂FI (M⁺): 279.9397; Found: 279.9397.

(7) 2-Iodobenzyl acetate 7g

\[
\begin{align*}
\text{I} & \quad \text{OH} + \quad \text{Ac}_2\text{O} \\
1.2 \text{ equiv.} & \quad \text{6 mol\% DMAP} \\
\text{CH}_2\text{Cl}_2, \text{rt}, 11 \text{ h} & \quad \text{Et}_3\text{N (1.5 equiv.)} \\
\end{align*}
\]

7g (94 %)

The reaction of (2-iodophenyl)methanol (3.95 g, 16.9 mmol), Ac₂O (2.07 g, 20.3 mmol), DMAP (0.13 g, 1.0 mmol), Et₃N (2.57 g, 25.4 mmol) and 50 mL of CH₂Cl₂ afforded 7g (4.39 g, 94 %): Liquid; ^1H NMR (300 MHz, CDCl₃) δ 7.84 (d, J = 7.8 Hz, 1 H), 7.41-7.30 (m, 2 H), 7.06-6.97 (m, 1 H), 5.11 (s, 2 H), 2.14 (s, 3 H); ^13C NMR (CDCl₃, 75 MHz) δ 170.4, 139.4, 138.2, 129.8, 129.3, 128.2, 98.3, 69.9, 20.8; MS (EI, m/z) 276 (M⁺, 19.32), 107 (100); IR (neat, cm⁻¹) 3060, 2953, 1737, 1468, 1438, 1379, 1361, 1221,
**Preparation of the alkynes.**

(1) 2-Ethynylphenyl acetate 8a

To a dried three-necked flask were added 2-iodophenyl acetate 7a (26.24 g, 100.2 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.70 g, 1.0 mmol), CuI (0.38 g, 2.0 mmol), and 60 mL of Et$_3$N under argon atmosphere. To the resulting mixture were added ethynyltrimethylsilane (14.72 g, 150.2 mmol) and 60 mL of dioxane. The mixture was stirred at 40 °C. After complete conversion of the starting materials as monitored by TLC, an aqueous HCl solution (1.0 M, 20 mL) and 100 mL water were added sequentially. The mixture was extracted with Et$_2$O (50 mL × 3). The organic layer was washed with 1.0 M HCl (50 mL × 3) and dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation gave a crude product 2-(2-(trimethylsilyl)ethynyl)phenyl acetate 9a (23.08 g) which was used directly in the next step.

To a three-necked flask were added sequentially 2-(2-(trimethylsilyl)ethynyl)phenyl acetate 9a (18.38 g), 120 mL of DMF and KF·2H$_2$O (13.18 g, 140.0 mmol). The mixture was stirred at room temperature. After complete conversion of the starting material as monitored by TLC, water (300 mL) was added. The mixture was extracted with Et$_2$O (100 mL × 3). The organic layer was washed with water (100 mL × 3) and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated. Chromatography on silica gel (eluent:
petroleum ether/ethyl acetate = 30/1) afforded 8a (9.37 g, 73 % by two steps): Liquid; 

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 7.5$ Hz, 1 H), 7.30 (t, $J = 7.8$ Hz, 1 H), 7.13 (t, $J = 7.7$ Hz, 1 H), 7.05 (d, $J = 8.1$ Hz, 1 H), 3.27 (s, 1 H), 2.26 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 168.4, 151.8, 133.2, 129.7, 125.6, 122.1, 116.0, 82.0, 78.3, 20.4; MS (EI, m/z) 160 (M$^+$, 8.81), 43 (100); IR (neat, cm$^{-1}$) 3284, 1760, 1484, 1446, 1369, 1199, 1173, 1099, 1035, 1010.

(2) 2-Ethynyl-4-methylphenyl acetate 8b

![Chemical structure](image)

The reaction of 7b (14.46 g, 52.4 mmol), ethynyltrimethylsilane (12.94 g, 132.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.37 g, 0.53 mmol), CuI (0.16 g, 0.84 mmol), and 200 mL of Et$_3$N afforded 9b as a crude product.

The reaction of 9b prepared above and KF·2H$_2$O (7.55 g, 80.3 mmol) in 200 mL of DMF afforded 8b (8.35 g, 92 % by two steps): Liquid; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 1.5$ Hz, 1 H), 7.17 (dd, $J = 8.4$ Hz, 1.8 Hz, 1 H), 6.97 (d, $J = 8.1$ Hz, 1 H), 3.21 (s, 1 H), 2.33 (s, 3 H), 2.32 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 169.1, 149.9, 135.7, 133.9, 130.8, 122.0, 115.8, 81.6, 78.7, 20.8, 20.6; MS (EI, m/z) 174 (M$^+$, 12.80), 132 (100); IR (neat, cm$^{-1}$) 3288, 1764, 1492, 1369, 1186, 1109, 1010.

(3) 2-Ethynyl-5-methylphenyl acetate 8c

![Chemical structure](image)

82 % by two steps
The reaction of 7c (5.52 g, 20.0 mmol), ethynyltrimethylsilane (4.00 g, 40.8 mmol), PdCl2(PPh3)2 (0.14 g, 0.20 mmol), CuI (0.06 g, 0.31 mmol), and 100 mL of Et3N afforded 9c as a crude product.

The reaction of 9c prepared above and KF·2H2O (2.82 g, 30.0 mmol) in 80 mL of DMF afforded 8c (2.87 g, 82 % by two steps): Liquid; 1H NMR (300 MHz, CDCl3) δ 7.42 (d, J = 7.8 Hz, 1 H), 7.01 (d, J = 8.1 Hz, 1 H), 6.91 (s, 1 H), 3.20 (s, 1 H), 2.36 (s, 3 H), 2.33 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 169.0, 152.0, 140.8, 133.3, 126.8, 122.9, 113.1, 81.2, 78.7, 21.4, 20.8; MS (EI, m/z) 174 (M+, 0.62), 43 (100); IR (neat, cm⁻¹) 3286, 2923, 1767, 1616, 1499, 1369, 1205, 1108, 1014; HRMS Calcd for C11H10O2 (M⁺): 174.0681; Found: 174.0681.

(4) 4-Chloro-2-ethynylphenyl acetate 8d

The reaction of 7d (10.34 g, 34.9 mmol), ethynyltrimethylsilane (8.60 g, 87.8 mmol), PdCl2(PPh3)2 (0.25 g, 0.36 mmol), CuI (0.089 g, 0.47 mmol), and 120 mL of Et3N afforded 9d as a crude product.

The reaction of 9d prepared above and KF·2H2O (4.94 g, 52.6 mmol) in 180 mL of DMF afforded 8d (6.06 g, 89 % by two steps): Liquid; 1H NMR (300 MHz, CDCl3) δ 7.51 (s, 1 H), 7.33 (d, J = 8.7 Hz, 1 H), 7.04 (d, J = 8.7 Hz, 1 H), 3.29 (s, 1 H), 2.34 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 168.6, 150.6, 133.2, 131.2, 130.1, 123.6, 117.8, 83.1, 20.8; MS (EI, m/z) 196 (M⁺(37Cl), 4.57), 194 (M⁺(35Cl), 10.31), 43 (100); IR (neat, cm⁻¹)
3263, 2922, 1752, 1482, 1376, 1216, 1173, 1012; HRMS Calcd for C\textsubscript{10}H\textsubscript{7}O\textsubscript{2}Cl (M\textsuperscript{+}(^{35}\text{Cl})): 194.0135; Found: 194.0138.

(5) 5-Chloro-2-ethynylphenyl acetate 8\text{e}

The reaction of 7\text{e} (16.32 g, 55.1 mmol), ethynyltrimethylsilane (8.30 g, 84.7 mmol), PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (0.35 g, 0.50 mmol), CuI (0.12 g, 0.63 mmol), and 150 mL of Et\textsubscript{3}N afforded 9\text{e} as a crude product.

The reaction of 9\text{e} and KF·2H\textsubscript{2}O (6.12 g, 65.1 mmol) in 80 mL of DMF afforded 8\text{e} (7.32 g, 68 % yield by two steps): Liquid; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.37 (d, \(J = 8.4\) Hz, 1 H), 7.11 (d, \(J = 8.4\) Hz, 1 H), 7.05 (s, 1 H), 3.21 (s, 1 H), 2.25 (s, 3 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) \(\delta\) 168.3, 152.4, 135.2, 134.1, 126.3, 123.0, 114.9, 82.9, 77.6, 20.7; MS (EI, m/z) 196 (M\textsuperscript{+}(^{37}\text{Cl}), 20.34), 194 (M\textsuperscript{+}(^{35}\text{Cl}), 61.15), 152 (100); IR (neat, cm\textsuperscript{-1}) 3264, 1761, 1597, 1560, 1480, 1403, 1369, 1197, 1175, 1117, 1077, 1010; HRMS Calcd for C\textsubscript{10}H\textsubscript{7}O\textsubscript{2}Cl (M\textsuperscript{+}(^{35}\text{Cl})): 194.0135; Found: 194.0132.

(6) 2-Ethynyl-5-fluorophenyl acetate 8\text{f}

The reaction of 7\text{f} (8.41 g, 30.0 mmol), ethynyltrimethylsilane (4.42 g, 45.1 mmol), PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (0.21 g, 0.30 mmol), CuI (0.11 g, 0.58 mmol), 20 mL of Et\textsubscript{3}N, and 20 mL of
dioxane afforded 9f as a crude product.

The reaction of 9f prepared above and KF·2H2O (4.60 g, 48.9 mmol) in 30 mL of DMF afforded 8f (4.57 g, 85 % yield by two steps): Liquid; 1H NMR (300 MHz, CDCl3) δ 7.51 (dd, J = 8.1 Hz, 6.6 Hz, 1 H), 6.99-6.83 (m, 2 H), 3.22 (s, 1 H), 2.34 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 168.1, 162.5 (d, J = 249.8 Hz), 153.0 (d, J = 11.3 Hz), 134.4 (d, J = 9.8 Hz), 113.1 (d, J = 21.8 Hz), 112.4 (d, J = 3.8 Hz), 110.5 (d, J = 24.8 Hz), 81.7 (d, J = 1.5 Hz), 77.5, 20.4; 19F NMR (282 MHz, CDCl3) δ -107.4; MS (EI, m/z) 178 (M+, 7.80), 43 (100); IR (neat, cm⁻¹) 3296, 1768, 1610, 1586, 1495, 1422, 1371, 1266, 1194, 1178, 1143, 1092, 1012; HRMS Calcd for C10H7O2F (M⁺): 178.0430; Found: 178.0429.

(7) 2-Ethynylbenzyl acetate 8g

The reaction of 7g (8.28 g, 30.0 mmol), ethynyltrimethylsilane (5.88 g, 60.0 mmol), PdCl2(PPh3)2 (1.05 g, 1.5 mmol), CuI (0.30 g, 1.6 mmol), and 30 mL of Et3N afforded 9g as a crude product.

The reaction of 9g prepared above and KF·2H2O (4.23 g, 45.0 mmol) in 100 mL of DMF afforded 8g (3.70 g, 71 % by two steps): Liquid; 1H NMR (300 MHz, CDCl3) δ 7.51 (d, J = 7.5 Hz, 1 H), 7.42-7.23 (m, 3 H), 5.27 (s, 2 H), 3.30 (s, 1 H), 2.11 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 170.8, 138.1, 132.9, 129.0, 128.2, 128.0, 121.4, 82.1, 80.7, 64.5, 20.8; MS (EI, m/z) 174 (M⁺, 8.11), 132 (100); IR (neat, cm⁻¹) 3287, 2922, 2852, 1738, 1596, 1487, 1439, 1373, 1231, 1032; HRMS Calcd for C11H10O2(M⁺): 174.0681; Found: 174.0679.
Preparation of the cyclopropene derivatives.

(1) Dimethyl 2-(2-acetoxyphenyl)cycloprop-2-ene-1,1-dicarboxylate \( \text{1a} \)

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{MeO}_2\text{C} \\
\text{CO}_2\text{Me} & \quad \text{CO}_2\text{Me} \\
+ & \quad + \\
\text{N}_2 & \quad \text{N}_2 \\
\text{CH}_2\text{Cl}_2, \text{reflux, 2.5 h} & \quad \text{0.25 mol% Rh}_2(\text{OAc})_4
\end{align*}
\]

To a dried Schlenk tube were added anhydrous \( \text{Rh}_2(\text{OAc})_4 \) (14.3 mg, 0.03 mmol,) and 10 mL of \( \text{CH}_2\text{Cl}_2 \) under argon atmosphere. After refluxing for 10 min, a solution of 2-ethynylphenyl acetate (6.00 g, 37.5 mmol) in 5 mL of \( \text{CH}_2\text{Cl}_2 \) was added. Then a solution of dimethyl diazomalonate (2.02 g, 12.8 mmol) in 10 mL of \( \text{CH}_2\text{Cl}_2 \) was added into the mixture via a syringe pump over a period of 2.5 hours. After complete conversion of the starting materials as monitored by TLC, the solvent was evaporated. Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) afforded \( \text{1a} \) (2.09 g, 56 %): Solid; mp 61-62 °C (petroleum ether/diethyl ether); \( ^1\text{H} \) NMR (300 MHz, \( \text{CDCl}_3 \)) \( \delta \) 7.60 (d, \( J = 7.5 \) Hz, 1 H), 7.44 (t, \( J = 7.4 \) Hz, 1 H), 7.28 (t, \( J = 7.4 \) Hz, 1 H), 7.20 (d, \( J = 8.1 \) Hz, 1 H), 6.93 (s, 1 H), 3.68 (s, 6 H), 2.32 (s, 3 H); \( ^{13}\text{C} \) NMR (\( \text{CDCl}_3 \), 75 MHz) \( \delta \) 170.6, 168.5, 149.9, 131.7, 131.6, 126.1, 123.0, 116.9, 108.3, 97.1, 52.2, 32.1, 20.8; MS (EI, m/z) 290 (M\(^+\), 4.45), 248 (100); IR (KBr, cm\(^{-1}\)) 3142, 2924, 2853, 1743, 1716, 1483, 1438, 1373, 1286, 1029, 1177, 1098, 1064, 1017; Elemental analysis Caled for \( \text{C}_{15}\text{H}_{14}\text{O}_6 \): C, 62.07; H, 4.86; Found: C, 62.15; H, 4.63.

(2) Methyl 2-(2-acetoxyphenyl)-1-phenylcycloprop-2-ene-carboxylate \( \text{1b} \)

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{CO}_2\text{Me} & \quad \text{CO}_2\text{Me} \\
+ & \quad + \\
\text{N}_2 & \quad \text{N}_2 \\
\text{CH}_2\text{Cl}_2, \text{reflux, 2.2 h} & \quad \text{0.27 mol% Rh}_2(\text{OAc})_4
\end{align*}
\]

S11
The reaction of 2-ethynylphenyl acetate (3.20 g, 20.0 mmol), methyl 
α-diazo-α-phenylacetate (0.88 g, 5.0 mmol), and Rh$_2$(OAc)$_4$ (6.0 mg, 0.014 mmol) in 15 
ml of CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 8/1 to 6/1) afforded 1b (1.33 g, 
86 %): Solid; mp 76-77 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) δ 
7.55 (d, $J$ = 7.5 Hz, 1 H), 7.38 (t, $J$ = 7.8 Hz, 1 H), 7.32-7.09 (m, 8 H), 3.64 (s, 3 H), 2.19 
(s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 174.6, 168.7, 149.9, 140.7, 131.3, 131.2, 128.1, 
128.0, 126.6, 126.3, 123.1, 118.6, 112.3, 103.2, 52.2, 32.8, 20.9; MS (EI, m/z) 308 (M$^+$), 
251 (100); IR (KBr, cm$^{-1}$) 3125, 2029, 2953, 1760, 1712, 1602, 1483, 1434, 1370, 1201, 
1176, 1096, 1037, 1015; Elemental analysis Calcd for C$_{19}$H$_{16}$O$_4$: C, 74.01; H, 5.23; 
Found: C, 73.84; H, 5.28.

(3) Ethyl 2-(2-acetoxyphenyl)-1-(phenylsulfonyl)cycloprop-2-enecarboxylate 1c

The reaction of 2-ethynylphenyl acetate (2.40 g, 15.0 mmol), ethyl 
α-diazo-α-phenylsulfonylacetate (0.68 g, 2.7 mmol), and Rh$_2$(OAc)$_4$ (6.0 mg, 0.014 mmol) 
in 10 mL of CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 4/1) afforded 1c (0.98 g, 
95 %): Solid; mp 106-107 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) 
δ 8.00 (d, $J$ = 7.5 Hz, 2 H), 7.65 (t, $J$ = 7.4 Hz, 1 H), 7.53 (t, $J$ = 7.5 Hz, 4 H), 7.35-7.24 
(m, 2 H), 7.10 (s, 1 H), 4.15 (q, $J$ = 7.1 Hz, 2 H), 2.32 (s, 3 H), 1.19 (t, $J$ = 7.1 Hz, 3 H); 
$^{13}$C NMR (CDCl$_3$, 75 MHz) δ 168.3, 167.2, 150.2, 139.8, 133.4, 132.5, 132.1, 129.3, 
128.6, 126.1, 123.0, 115.7, 109.3, 97.4, 62.0, 51.5, 20.9, 13.9; MS (EI, m/z) 386 (M$^+$, 
0.11), 245 (100); IR (KBr, cm$^{-1}$) 3132, 2983, 2925, 2853, 1765, 1729, 1560, 1482, 1447, 

s12
1370, 1307, 1256, 1181, 1081, 1018; Elemental analysis Calcd for C_{20}H_{18}O_{6}S: C, 62.16; H, 4.70; S, 8.30; Found: C, 62.40; H, 4.33; S, 7.91.

(4) Dimethyl 2-(2-acetoxy-5-methylphenyl)cycloprop-2-ene-1,1-dicarboxylate 1d

\[ \text{MeO}_2\text{C}\text{CO}_2\text{Me} + \text{MeO}_2\text{C}\text{CO}_2\text{Me} \xrightarrow{0.43 \text{ mol}\% \text{ Rh}_2(\text{OAc})_4} \text{MeO}_2\text{C}\text{N}_2 \xrightarrow{\text{CH}_2\text{Cl}_2, \text{reflux, 2.5 h}} \text{MeO}_2\text{C}\text{CO}_2\text{Me} + \text{MeO}_2\text{C}\text{CO}_2\text{Me} \]

The reaction of 2-ethynyl-4-methylphenyl acetate (8.35 g, 48.0 mmol), dimethyl diazomalonate (1.58 g, 10.0 mmol), and Rh_{2}(OAc)_{4} (19.0 mg, 0.043 mmol) in 26 mL of CH_{2}Cl_{2} (eluent: petroleum ether/ethyl acetate = 15/1 to 6/1) afforded 1d (1.98 g, 65 %):

Solid; mp 69-70 °C (petroleum ether/diethyl ether); \(^1^H\) NMR (300 MHz, CDCl_{3}) \(\delta \) 7.42 (s, 1 H), 7.26 (dd, \(J = 4.8 \text{ Hz}, 3.6 \text{ Hz}, 1 \text{ H} \)), 7.10 (d, \(J = 8.4 \text{ Hz}, 1 \text{ H} \)), 6.89 (s, 1 H), 3.72 (s, 6 H), 2.37 (s, 3 H), 2.34 (s, 3 H); \(^{13}\)C NMR (CDCl_{3}, 75 MHz) \(\delta \) 170.8, 168.9, 147.8, 136.1, 132.5, 132.0, 122.8, 116.5, 108.4, 96.9, 52.4, 32.1, 20.9, 20.7; MS (EI, m/z) 304 (M\(^+\), 20.38), 262 (100); IR (KBr, cm\(^{-1}\)) 3270, 3141, 2956, 2851, 1761, 1604, 1493, 1438, 1369, 1252, 1191, 1067, 1015; Elemental analysis Calcd for C_{16}H_{16}O_{6}: C, 63.15; H, 5.30; Found: C, 62.81; H, 5.42.

(5) Dimethyl 2-(2-acetoxy-4-methylphenyl)cycloprop-2-ene-1,1-dicarboxylate 1e

\[ \text{MeO}_2\text{C}\text{CO}_2\text{Me} + \text{MeO}_2\text{C}\text{CO}_2\text{Me} \xrightarrow{0.42 \text{ mol}\% \text{ Rh}_2(\text{OAc})_4} \text{MeO}_2\text{C}\text{N}_2 \xrightarrow{\text{CH}_2\text{Cl}_2, \text{reflux, 2 h}} \text{MeO}_2\text{C}\text{CO}_2\text{Me} + \text{MeO}_2\text{C}\text{CO}_2\text{Me} \]

The reaction of 2-ethynyl-5-methylphenyl acetate (2.87 g, 16.5 mmol), dimethyl diazomalonate (0.87 g, 5.5 mmol), and Rh_{2}(OAc)_{4} (10.0 mg, 0.023 mmol) in 15 mL of
CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 5/1) afforded $1e$ (0.92 g, 55 %): Solid; mp 93-94 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J$ = 7.8 Hz, 1 H), 7.11 (d, $J$ = 7.5 Hz, 1 H), 7.04 (s, 1 H), 6.84 (s, 1 H), 3.70 (s, 6 H), 2.39 (s, 3 H), 2.34 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 170.9, 168.7, 149.9, 142.9, 131.6, 127.1, 123.6, 114.2, 108.3, 95.8, 52.3, 32.1, 21.6, 21.0; MS (EI, m/z) 304 (M$^+$, 18.14), 262 (100); IR (KBr, cm$^{-1}$) 3136, 2955, 2849, 1769, 1732, 1615, 1499, 1436, 1372, 1195, 1149, 1113, 1065, 1017; Elemental analysis Calcd for C$_{16}$H$_{16}$O$_6$: C, 63.15; H, 5.30; Found: C, 63.18; H, 5.46.

(6) Dimethyl 2-(2-acetoxy-5-chlorophenyl)cycloprop-2-ene-1,1-dicarboxylate $1f$

The reaction of 4-chloro-2-ethynylphenyl acetate (6.04 g, 31.1 mmol), dimethyl diazomalonate (1.58 g, 10.0 mmol), and Rh$_2$(OAc)$_4$ (20.0 mg, 0.045 mmol) in 30 mL of CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 5/1) afforded $1f$ (2.09 g, 65 %): Solid; mp 104-105 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.60 (s, 1 H), 7.42 (dd, $J$ = 8.7 Hz, 0.9 Hz, 1 H), 7.19 (d, $J$ = 8.7 Hz, 1 H), 7.00 (s, 1 H), 3.73 (s, 6 H), 2.35 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 170.4, 168.4, 148.4, 131.6, 131.2, 124.4, 118.6, 107.8, 98.9, 52.5, 32.4, 20.9; MS (EI, m/z) 326 (M$^+$ (37Cl), 1.11), 324 (M$^+$ (35Cl), 3.17), 282 (100); IR (KBr, cm$^{-1}$) 3142, 2952, 1755, 1725, 1483, 1440, 1374, 1253, 1198, 1181, 1116, 1060, 1013; Elemental analysis Calcd for C$_{15}$H$_{13}$ClO$_6$: C, 55.48; H, 4.04; Found: C, 55.17; H, 4.07.

(7) Ethyl 2-(2-acetoxy-5-chlorophenyl)-1-(phenylsulfonyl)cycloprop-2-ene-1-carboxylate
The reaction of 4-chloro-2-ethynylphenyl acetate (4.32 g, 22.3 mmol), ethyl 2-diazo-2-benzenesulfonylacetate (1.92 g, 7.6 mmol), and Rh$_2$(OAc)$_4$ (11.0 mg, 0.025 mmol) in 20 mL of CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 4/1) afforded 1g (2.62 g, 83 %): Solid; mp 119-120 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J$ = 7.8 Hz, 2 H), 7.65 (t, $J$ = 7.2 Hz, 1 H), 7.52 (t, $J$ = 7.5 Hz, 2 H), 7.48-7.36 (m, 2 H), 7.25 (d, $J$ = 9.0 Hz, 1 H), 7.15 (s, 1 H), 4.14 (q, $J$ = 7.1 Hz, 2 H), 2.29 (s, 3 H), 1.18 (t, $J$ = 7.1 Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 168.1, 166.9, 148.6, 139.7, 133.6, 132.3, 131.4, 131.3, 129.3, 128.7, 124.4, 117.2, 108.6, 99.0, 62.1, 51.5, 20.8, 13.8; MS (EI, m/z) 422 (M$^+$ (37Cl), 0.09), 420 (M$^+$ (35Cl), 0.20), 279 (100); IR (KBr, cm$^{-1}$) 3131, 2985, 2923, 1770, 1728, 1479, 1444, 1371, 1309, 1257, 1178, 1152, 1087, 1019; Elemental analysis Calcd for C$_{20}$H$_{17}$ClO$_6$S: C, 57.08; H, 4.07; S, 7.62; Found: C, 57.06; H, 4.07; S, 7.89.

(8) Dimethyl 2-(2-acetoxy-4-chlorophenyl)cycloprop-2-ene-1,1-dicarboxylate 1h

The reaction of 5-chloro-2-ethynylphenyl acetate (5.82 g, 30.0 mmol), dimethyl diazomalonate (1.26 g, 8.0 mmol), and Rh$_2$(OAc)$_4$ (9.2 mg, 0.021 mmol) in 25 mL of CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 5/1) afforded 1h (1.48 g, 57 %): Solid;
mp 99-100 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 9.0\) Hz, 1 H), 7.27-7.18 (m, 2 H), 6.89 (s, 1 H), 3.65 (s, 6 H), 2.29 (s, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 170.6, 168.2, 150.2, 137.2, 132.4, 126.6, 123.7, 115.7, 107.7, 97.7, 52.4, 32.1, 20.9; MS (EI, m/z) 326 (M\(^{+}\)\(^{37}\)Cl), 1.80), 324 (M\(^{+}\)\(^{35}\)Cl), 4.95), 282 (100); IR (KBr, cm\(^{-1}\)) 2956, 2922, 2854, 1775, 1728, 1595, 1461, 1373, 1286, 1181, 1066; Elemental analysis Calcd for C\(_{15}\)H\(_{13}\)ClO\(_6\): C, 55.48; H, 4.04; Found: C, 55.33; H, 4.12.

(9) Methyl 2-(2-acetoxy-4-chlorophenyl)-1-phenylcycloprop-2-ene carboxylate \(\text{1i}\)

![Methyl 2-(2-acetoxy-4-chlorophenyl)-1-phenylcycloprop-2-ene carboxylate](image)

The reaction of 5-chloro-2-ethynylphenyl acetate (5.82 g, 30.0 mmol), methyl \(\alpha\)-diazo-\(\alpha\)-phenylacetate (1.41 g, 8.0 mmol), and Rh\(_2\)(OAc)$_4$ (9.7 mg, 0.022 mmol) in 25 mL of CH\(_2\)Cl\(_2\) (eluent: petroleum ether/ethyl acetate = 8/1) afforded \(\text{1i}\) (1.65 g, 60 %):
Solid; mp 99-100 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.58-7.52 (m, 1 H), 7.37-7.18 (m, 8 H), 3.72 (s, 3 H), 2.25 (s, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 174.2, 168.2, 150.0, 140.3, 136.4, 131.8, 128.0, 127.9, 126.6, 123.7, 117.3, 111.5, 103.6, 52.1, 32.7, 20.7; MS (EI, m/z) 344 (M\(^{+}\)\(^{37}\)Cl), 3.63), 342 (M\(^{+}\)\(^{35}\)Cl), 10.46), 285 (100); IR (KBr, cm\(^{-1}\)) 2956, 2923, 2849, 1771, 1716, 1594, 1563, 1469, 1399, 1370, 1287, 1179, 1075, 1011; Elemental analysis Calcd for C\(_{19}\)H\(_{15}\)ClO\(_4\): C, 66.58; H, 4.41; Found: C, 66.32; H, 4.46.

(10) Dimethyl 2-(2-acetoxy-4-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate \(\text{1j}\)
The reaction of 2-ethynyl-5-fluorophenyl acetate (4.57 g, 25.7 mmol), dimethyl diazomalonate (1.26 g, 8.0 mmol), and Rh$_2$(OAc)$_4$ (9.4 mg, 0.021 mmol) in 25 mL of CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 4/1) afforded 1j (1.42 g, 58 %): Solid; mp 97-98 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.61 (dd, $J$ = 9.2 Hz, 6.2 Hz, 1 H), 7.09-6.98 (m, 2 H), 6.90 (s, 1 H), 3.72 (s, 6 H), 2.35 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 170.7, 168.1, 165.6, 162.2, 151.0 (d, $J$ = 11.3 Hz), 133.0 (d, $J$ = 9.8 Hz), 113.67 (d, $J$ = 21.8 Hz), 111.3 (d, $J$ = 25.5 Hz), 107.8, 96.5, 52.4, 32.1, 20.9; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -105.2; MS (EI, m/z) 308 (M$^+$, 4.73), 266 (100); IR (KBr, cm$^{-1}$) 2955, 2851, 1750, 1604, 1497, 1438, 1370, 1272, 1196, 1144, 1068, 1019; Elemental analysis Calcd for C$_{15}$H$_{13}$FO$_6$: C, 58.44; H, 4.25; Found: C, 58.79; H, 4.34.

(11) Dimethyl 2-(2-(acetoxymethyl)phenyl)cycloprop-2-ene-1,1-dicarboxylate 4k

The reaction of 2-ethynylbenzyl acetate (3.65 g, 21.0 mmol), dimethyl diazomalonate (1.11 g, 7.0 mmol), and Rh$_2$(OAc)$_4$ (8.2 mg, 0.019 mmol) in 25 mL of CH$_2$Cl$_2$ (eluent: petroleum ether/ethyl acetate = 4/1) afforded 4k (1.05 g, 49 %): Liquid; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.61-7.37 (m, 4 H), 7.00 (s, 1 H), 5.34 (s, 2 H), 3.73 (s, 6 H), 2.13 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 170.9, 170.7, 137.0, 131.4, 130.8, 128.9, 128.7, 122.5,
110.1, 98.4, 63.7, 52.5, 32.1, 20.8; MS (EI, m/z) 304 (M⁺, 30.3), 115 (100); IR (neat, cm⁻¹) 3133, 2951, 1738, 1437, 1390, 1289, 1231, 1144, 1083; HRMS Calcd for C₁₆H₁₆O₆(M⁺): 304.0947; Found: 304.0942.

(12) Methyl 2-(2-(acetoxymethyl)phenyl)-1-phenylcyclopenta-2-ene carboxylate 4l

The reaction of 2-ethynylbenzyl acetate (2.75 g, 16.0 mmol), methyl α-diazo-α-phenylacetate (0.88 g, 5.0 mmol) and Rh₂(OAc)₄ (6.1 mg, 0.014 mmol) in 20 mL of CH₂Cl₂ (eluent: petroleum ether/ethyl acetate = 7/1) afforded 4l (1.08 g, 67 %). Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.44 (dd, J = 15.5 Hz, 7.1 Hz, 2 H), 7.36-7.08 (m, 8 H), 5.33-5.21 (m, 2 H), 3.63 (s, 3 H), 2.02 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 174.6, 170.7, 140.4, 136.8, 130.7, 130.1, 128.8, 128.5, 128.04, 128.01, 126.5, 123.8, 114.9, 103.4, 63.8, 52.2, 32.7, 20.7; MS (EI, m/z) 322 (M⁺, 15.81), 203 (100); IR (neat, cm⁻¹) 3130, 2951, 1722, 1491, 1438, 1380, 1228, 1025; HRMS Calcd for C₂₀H₁₈O₄(M⁺): 322.1205; Found: 322.1205.

**Synthesis of Benzofurans and Isochromenes.**

(1) 3-(Bis(methoxycarbonyl)methyl)benzofuran 2a
Typical procedure: To a dried Schlenk tube were added 1.0 mL of THF and \( n\)-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) under argon atmosphere. The solution was cooled to -60°C. A solution of 1a (72.8 mg, 0.25 mmol) in THF (3 mL) was added dropwise with a syringe within 10 min. The resulting mixture was stirred at -60 °C for another 55 min as monitored by TLC, quenched with a saturated aqueous NH₄Cl solution (0.5 mL) and 10 mL of water. The mixture was extracted with Et₂O (10 mL × 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7/1) afforded the product 2a (44.8 mg, 72%): Solid; mp 49-50 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) 7.82 (s, 1 H), 7.61 (d, \( J = 7.2 \) Hz, 1 H), 7.48 (m, \( J = 7.5 \) Hz, 1 H), 7.35-7.22 (m, 2 H), 4.87 (s, 1 H), 3.78 (s, 6 H); \(^{13}\)C NMR (CDCl₃, 75 MHz) \( \delta \) 167.7, 155.0, 143.9, 126.4, 124.6, 122.8, 120.1, 112.3, 111.5, 52.9, 48.2; MS (GC, m/z) 248 (M⁺, 88.13), 161 (100); IR (KBr, cm⁻¹) 2956, 2865, 1740, 1447, 1371, 1264, 1246, 1228, 1201, 1123, 1115, 52.9, 48.2; Elemental analysis Calcd for C₁₃H₁₂O₅: C, 62.90; H, 4.87; Found: C, 62.96; H, 4.79.

(2) 3-(Phenyl(methoxycarbonyl)methyl)benzofuran 2b

\[
\begin{align*}
\text{Ph} & \quad \text{CO₂Me} \\
\text{OAc} & \quad \text{Ph} \\
& \quad \text{CO₂Me}
\end{align*}
\]

![Diagram](https://via.placeholder.com/150)

The reaction of 1b (77.2 mg, 0.25 mmol) in THF (3 mL) and \( n\)-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) in THF (1.0 mL) afforded 2b (32.3 mg, 48%) (eluent: petroleum ether/ethyl acetate = 50/1): Solid; mp 79-80 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) 7.68 (s, 1 H), 7.49-7.38 (m, 3 H), 7.37-7.22 (m, 5 H), 7.15 ( t, \( J = 7.5 \) Hz, 1 H), 5.11 (s, 1 H), 3.76 (s, 3 H); \(^{13}\)C NMR (CDCl₃, 75 MHz) \( \delta \) 172.2, 155.3,
143.2, 136.9, 128.7, 127.7, 126.9, 124.5, 122.6, 119.8, 118.0, 111.5, 52.5, 47.8;
MS (EI, m/z) 266 (M⁺, 31.58), 207 (100); IR (KBr, cm⁻¹) 3066, 3028, 2954, 2842, 1736, 1631, 1492, 1445, 1318, 1200, 1152, 1003; Elemental analysis Calcd for C₁₇H₁₄O₃: C, 76.68; H, 5.30; Found: C, 76.81; H, 5.28.

(3) 3-(Phenylsulfonyl(methoxycarbonyl)methyl)benzofuran 2c

\[
\begin{align*}
\text{PhO}_2S & \quad \text{CO}_2\text{Et} \\
\text{OAc} & \quad \text{n-BuLi (4.0 equiv)} \quad \text{THF, -60 °C, (12+44) min} \quad \text{PhO}_2S & \quad \text{CO}_2\text{Et} \\
\text{1c} & \quad \text{2c (44 %)}
\end{align*}
\]

The reaction of 1c (95.7 mg, 0.25 mmol) in THF (3.0 mL) and n-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) in THF (1.0 mL) afforded 2c (37.6 mg, 44%), eluent: petroleum ether/diethyl ether = 3/1); Solid; mp 103-104 °C (petroleum ether/diethyl ether); ¹H NMR (300 MHz, CDCl₃) δ 7.69-7.53 (m, 5 H), 7.49-7.37 (m, 3 H), 7.31 (td, J = 7.6 Hz, 1.2 Hz, 1 H), 7.23 (td, J = 7.5 Hz, 1.2 Hz, 1 H), 5.39 (s, 1 H), 4.34-4.16 (m, 2 H), 1.26 (t, J = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.5, 154.7, 146.2, 135.6, 134.3, 129.7, 128.6, 125.9, 125.0, 123.3, 120.1, 111.5, 108.8, 67.4, 62.8, 13.8; MS (EI, m/z) 344 (M⁺, 7.22), 203 (100); IR (KBr, cm⁻¹) 2983, 2924, 2853, 1740, 1529, 1450, 1376, 1328, 1267, 1151, 1116, 1080, 1019; Elemental analysis Calcd for C₁₈H₁₆O₅S: C, 62.78; H, 4.68; S, 9.32; Found: C, 62.98; H, 4.71; S, 9.32.

(4) 5-Methyl-3-(bis(methoxycarbonyl)methyl)benzofuran 2d

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{OAc} & \quad \text{n-BuLi (4.0 equiv)} \quad \text{THF, -60 °C, (11+45) min} \quad \text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{1d} & \quad \text{2d (53 %)}
\end{align*}
\]

The reaction of 1d (76.2 mg, 0.25 mmol) in THF (2.0 mL) and n-BuLi (2.5 M in
hexane, 0.4 mL, 1.0 mmol) in THF (1.0 mL) afforded 2d (34.6 mg, 53%) (eluuent: petroleum ether/ethyl acetate = 15/1): Solid; mp 94-95 °C (petroleum ether/diethyl ether); 1H NMR (300 MHz, CDCl3) δ 7.78 (s, 1 H), 7.37 (d, J = 8.7 Hz, 2 H), 7.12 (dd, J = 8.7 Hz, 1.5 Hz, 1 H), 4.84 (s, 1 H), 3.79 (s, 6 H), 2.45 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 167.8, 153.6, 144.1, 132.4, 126.5, 126.0, 119.8, 112.1, 111.1, 53.0, 48.2, 21.4; MS (EI, m/z) 262 (M^+, 20.14), 41 (100); IR (KBr, cm⁻¹) 2955, 2921, 2850, 1738, 1589, 1462, 1434, 1373, 1265, 1217, 1149, 1106, 1063, 1020; Elemental analysis Calcd for C₁₄H₁₄O₅: C, 64.12; H, 5.38; Found: C, 64.06; H, 5.55.

(5) 6-Methyl-3-(bis(methoxycarbonyl)methyl)benzofuran 2e

The reaction of 1e (76.1 mg, 0.25 mmol) in THF (3.0 mL) and n-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) in THF (1.0 mL) afforded 2e (44.0 mg, 67%) (eluuent: petroleum ether/diethyl ether = 5/1): Solid; mp 53-54 °C (petroleum ether/diethyl ether); 1H NMR (300 MHz, CDCl3) δ 7.75 (s, 1 H), 7.49 (d, J = 8.1 Hz, 1 H), 7.30 (s, 1 H), 7.20 (dd, J = 8.0 Hz, 0.8 Hz, 1 H), 4.85 (s, 1 H), 3.78 (s, 6 H), 2.47 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 167.8, 155.5, 143.3, 135.0, 124.3, 124.0, 119.6, 112.3, 111.7, 52.9, 48.3, 21.5; MS (EI, m/z) 262 (M^+, 27.48), 57 (100); IR (KBr, cm⁻¹) 2955, 2921, 2850, 1741, 1623, 1494, 1436, 1373, 1305, 1222, 1140, 1101, 1069, 1022; Elemental analysis Calcd for C₁₄H₁₄O₅: C, 64.12; H, 5.38; Found: C, 63.82; H, 5.44.

(6) 5-Chloro-3-(bis(methoxycarbonyl)methyl)benzofuran 2f
The reaction of 1f (81.1 mg, 0.25 mmol) in THF (3.0 mL) and n-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) in THF (1.0 mL) afforded 2f (47.2 mg, 67%) (eluent: petroleum ether/diethyl ether = 5/1): Solid; mp 95-96 °C (petroleum ether/diethyl ether); 1H NMR (300 MHz, CDCl3) δ 7.83 (s, 1 H), 7.60 (d, J = 2.1 Hz, 1 H), 7.41 (d, J = 8.7 Hz, 1 H), 7.27 (dd, J = 9.0 Hz, 2.1 Hz, 1 H), 4.81 (s, 1 H), 3.80 (s, 6 H); 13C NMR (CDCl3, 75 MHz) δ 167.5, 153.5, 145.3, 128.7, 127.9, 125.0, 120.1, 112.6, 112.2, 53.1, 48.1; MS (EI, m/z) 284 (M+ (37Cl), 5.73), 282 (M+ (35Cl), 15.05), 59 (100); IR (KBr, cm⁻¹) 2958, 2851, 1740, 1611, 1496, 1466, 1429, 1299, 1260, 1198, 1158, 1099, 1009; Elemental analysis Calcld for C13H11ClO5: C, 55.24; H, 3.92; Found: C, 55.31; H, 4.07.

(7) 5-Chloro-3-(phenylsulfonyl(methoxycarbonyl)methyl)benzofuran 2g

The reaction of 1g (84.0 mg, 0.20 mmol) in THF (3.0 mL) and n-BuLi (2.5 M in hexane, 0.32 mL, 0.8 mmol) in THF (1.0 mL) afforded 2g (44.6 mg, 59%) (eluent: petroleum ether/ethyl acetate = 7/1): Solid; mp 125-126 °C (petroleum ether/diethyl ether); 1H NMR (300 MHz, CDCl3) δ 7.74 (s, 1 H), 7.73-7.60 (m, 3 H), 7.50-7.36 (m, 4 H), 7.25 (dd, J = 9.0 Hz, 2.1 Hz, 1 H), 5.31 (s, 1 H), 4.33-4.16 (m, 2 H), 1.26 (t, J = 7.2 Hz, 3 H); 13C NMR (CDCl3, 75 MHz) δ 164.2, 153.2, 147.7, 135.7, 134.5, 129.8, 129.1, 128.8, 127.3, 125.4, 120.0, 112.6, 108.7, 67.4, 63.0, 13.8; MS (EI, m/z) 380 (M+ (37Cl), 2.22),
378 (M$^+$ ($^{35}$Cl), 6.08), 237 (100); IR (KBr, cm$^{-1}$) 2926, 2856, 1739, 1580, 1451, 1327, 1269, 1152, 1082, 1019; Elemental analysis Calcd for C$_{13}$H$_{15}$ClO$_5$S: C, 57.07; H, 3.99; S, 8.46; Found: C, 57.33; H, 4.09; S, 8.70.

(8) 6-Chloro-3-(bis(methoxycarbonyl)methyl)benzofuran 2h

\[
\begin{array}{c}
\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
\text{Cl}
\end{array}
\quad \xrightarrow{n\text{-BuLi (4.0 equiv)}}
\quad \begin{array}{c}
\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
\text{Cl}
\end{array}
\]

The reaction of 1h (81.3 mg, 0.25 mmol) in THF (3.0 mL) and n-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) in THF(1.0 mL) afforded 2h (42.8 mg, 60%) (eluent: petroleum ether/diethyl ether = 7/1): Solid; mp 58-59 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1 H), 7.58-7.48 (m, 2 H), 7.25 (d, $J = 8.4$ Hz, 1 H), 4.83 (s, 1 H), 3.78 (s, 6 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 167.5, 155.2, 144.6, 130.6, 125.2, 123.7, 121.0, 112.5, 112.1, 53.0, 48.2; MS (EI, m/z) 284 (M$^+$ ($^{37}$Cl), 5.75), 282 (M$^+$ ($^{35}$Cl), 13.98), 59 (100); IR (KBr, cm$^{-1}$) 2956, 2861, 1803, 1748, 1597, 1465, 1371, 1259, 1155, 1107, 1022; Elemental analysis Calcd for C$_{13}$H$_{11}$ClO$_5$: C, 55.24; H, 3.92; Found: C, 55.22; H, 4.01.

(9) 6-Chloro-3-(phenyl(methoxycarbonyl)methyl)benzofuran 2i

\[
\begin{array}{c}
\text{Ph} \quad \text{CO}_2\text{Me} \\
\text{Cl}
\end{array}
\quad \xrightarrow{n\text{-BuLi (4.0 equiv)}}
\quad \begin{array}{c}
\text{Ph} \quad \text{CO}_2\text{Me} \\
\text{Cl}
\end{array}
\]

The reaction of 1i (68.6 mg, 0.20 mmol) in THF (3.0 mL) and n-BuLi (2.5 M in hexane, 0.32 mL, 0.8 mmol) in THF (1.0 mL) afforded 2i (38.7 mg, 64%) (eluent: petroleum ether/ethyl acetate = 50/1): Solid; mp 83-84 °C (petroleum ether/diethyl ether);
1H NMR (400 MHz, CDCl3) δ 7.68 (d, J = 1.2 Hz, 1 H), 7.47 (d, J = 1.5 Hz, 1 H), 7.41-7.27 (m, 5 H), 7.20 (d, J = 8.4 Hz, 1 H), 7.12 (dd, J = 8.3 Hz, 1.7 Hz, 1 H), 5.07 (s, 1 H), 3.75 (s, 3 H); 13C NMR (CDCl3, 100 MHz) δ 171.9, 155.3, 143.9, 136.5, 130.4, 128.8, 128.2, 127.8, 125.6, 123.4, 120.5, 118.0, 112.1, 52.5, 47.7; MS (EI, m/z) 302 (M+ (37Cl), 8.51), 300 (M+ (35Cl), 24.43), 241 (100); IR (KBr, cm⁻¹) 3067, 2955, 2864, 1739, 1604, 1463, 1298, 1158, 1099, 1001; Elemental analysis Calcd for C17H13ClO3: C, 67.89; H, 4.36; Found: C, 67.87; H, 4.57.

(10) 6-Fluoro-3-(bis(methoxycarbonyl)methyl)benzofuran 2j

![Conversion of 1j to 2j](image)

The reaction of 1j (77.1 mg, 0.25 mmol) in 3.0 mL of THF and n-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) in THF (1.0 mL) afforded 2j (46.1 mg, 69%) (eluent: petroleum ether/ethyl acetate = 10/1): Solid; mp 71-72 °C (petroleum ether/diethyl ether); 1H NMR (300 MHz, CDCl3) δ 7.80 (s, 1 H), 7.55 (dd, J = 8.7 Hz, 5.4 Hz, 1 H), 7.20 (dd, J = 8.9 Hz, 2.3 Hz, 1 H), 7.03 (td, J = 8.9 Hz, 2.1 Hz, 1 H), 4.83 (s, 1 H), 3.79 (s, 6 H); 13C NMR (CDCl3, 75 MHz) δ 167.6, 161.0 (d, J = 241.5 Hz), 155.1 (d, J = 13.4 Hz), 144.5 (d, J = 4.6 Hz), 122.7, 120.8 (d, J = 9.9 Hz), 112.4, 111.4 (d, J = 23.9 Hz), 99.3 (d, J = 27.1 Hz), 53.1, 48.2; 19F NMR (282 MHz, CDCl3) δ -116.9; MS (EI, m/z) 266 (M+, 93.9), 179 (100); IR (KBr, cm⁻¹) 2957, 2852, 1747, 1616, 1490, 1438, 1373, 1301, 1216, 1141, 1078, 1020; Elemental analysis Calcd for C13H11O5F: C, 58.65; H, 4.16; F, 7.14; Found: C, 58.44; H, 4.25; F, 7.01.

(11) 3-(Di(methoxycarbonyl)methyl)isochromene 4k
The reaction of 3k (76.3 mg, 0.25 mmol) in THF (3.0 mL) and n-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) in THF (1.0 mL) afforded 4k (35.8 mg, 54%) (eluent: petroleum ether/ethyl acetate = 8/1): Solid; mp 73-74 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.30-7.14 (m, 2 H), 7.10-6.99 (m, 2 H), 6.75 (s, 1 H), 5.06 (s, 2 H), 4.53 (s, 1 H), 3.77 (s, 6 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 168.6, 147.1, 129.8, 128.2, 127.9, 127.0, 124.2, 120.0, 109.3, 68.3, 52.9, 50.7; MS (EI, m/z) 262 (M\(^+\), 85.49), 115 (100); IR (KBr, cm\(^{-1}\)) 2955, 2846, 1741, 1630, 1442, 1324, 1260, 1152, 1024; Elemental analysis Caled for C\(_{14}\)H\(_{14}\)O\(_5\): C, 64.12; H, 5.38; Found: C, 64.13; H, 5.40.

(12) 3-(Phenyl(methoxycarbonyl)methyl)isochromene 4l

The reaction of 3l (81.7 mg, 0.25 mmol) in THF (3.0 mL) and n-BuLi (2.4 M in hexane, 0.42 mL, 1.0 mmol) in THF (1.0 mL) afforded 4l (36.8 mg, 52%) (eluent: petroleum ether/ethyl acetate = 50/1): Liquid; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.41-7.11 (m, 7 H), 7.01 (d, \(J = 7.2\) Hz, 2 H), 6.40 (s, 1 H), 5.03 (s, 2 H), 4.90 (s, 1 H), 3.72 (s, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 172.8, 146.3, 136.3, 130.7, 128.7, 128.4, 128.1, 127.6, 126.9, 124.1, 120.0, 114.4, 68.2, 52.4, 50.3; MS (EI, m/z) 280 (M\(^+\), 75.75), 115 (100); IR (neat, cm\(^{-1}\)) 3066, 3031, 2951, 2853, 1784, 1735, 1631, 1602, 1493, 1453, 1356, 1275,
Deuterium Experiment

Deuterated 3-(bis(methoxycarbonyl)methyl)benzofuran 2a-d

To a dried Schlenk tube were added 1.0 mL of THF and n-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) under argon atmosphere. The solution was cooled to -60 °C. A solution of 1a (72.8 mg, 0.25 mmol) in THF (2.5 mL) was added dropwise with a syringe within 18 min. The resulting mixture was stirred at -60 °C for another 45 min. A solution of AcOD (91.0 mg, 1.5 mmol) in 0.5 mL of THF was added. The mixture was stirred for 22 min at -60 °C and then at room temperature for additional 30 min. D₂O (5 mL) was added. The mixture was extracted with Et₂O (5 mL x 3) and the organic layer was dried over anhydrous MgSO₄ for 5 min. Filtration and evaporation of the solvent gave a crude product 2a-dd (98% deuteration on sp³ carbon and 70% deuteration on 2-position of the furan moiety). Flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1) afforded 2a-d (22.8 mg, 36% yield, 70% deuteration on the 2-position of the furan moiety): liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.82 (s, 0.29 H), 7.65-7.59 (m, 1 H), 7.52-7.46 (m, 1 H), 7.36-7.22 (m, 2 H), 4.87 (s, 1 H), 3.78 (s, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.8, 155.1 (d, J = 4.6 Hz), 143.9, 126.5, 124.6, 122.9, 120.1, 112.3 (d, J = 14.6 Hz), 111.6, 53.0, 48.2; MS (crude product) (EI, m/z) 250 (M⁺, 9.05), 59 (100); IR (neat, cm⁻¹) 2957, 2927, 2854, 1738, 1614, 1450, 1436, 1264, 1229, 1156, 1109, 1076, 1017; HRMS (crude product) Calcd for C₁₃H₁₀D₂O₅ (M⁺): 250.0810, found: 250.0809.
Preparation of Aryl Substituted Benzofurans.

(1) Dimethyl 2-(5-phenylbenzofuran-3-yl)malonate 5fa

Typical procedure: To a dried Schlenk tube were added K$_3$PO$_4$ (63.8 mg, 0.30 mmol) under argon atmosphere. The tube was dried with hot airflow under vacuum and backfilled with argon for three times. Then Pd(OAc)$_2$ (1.1 mg, 0.0049 mmol), LB-phos·HBF$_4$ (4.1 mg, 0.0091 mmol), phenylboronic acid (36.8 mg, 0.30), and 1.0 mL of dioxane were added sequentially to the Schlenk tube. After being stirred for about 5 min at room temperature, 2f (42.1 mg, 0.15 mmol), another 1.0 mL of dioxane, and 8.0 μL of water (8.0 mg, 0.44 mmol) were added sequentially. The resulting mixture was heated at 80 °C with a preheated oil bath. After 6 h, the reaction was complete as monitored by TLC. The reaction mixture was then cooled and filtered through a short column of silica gel (eluent: 2×10 mL of CH$_2$Cl$_2$). Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) afforded 5fa (40.7 mg, 84%): Liquid; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.87 (s, 1 H), 7.82 (t, $J$ = 1.2 Hz, 1 H), 7.66-7.60 (m, 2 H), 7.56 (d, $J$ = 1.5 Hz, 2 H), 7.51-7.43 (m, 2 H), 7.40-7.33 (m, 1 H), 4.93 (s, 1 H), 3.81 (s, 6 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 167.7, 154.7, 144.6, 141.5, 136.7, 128.7, 127.5, 127.0, 126.9, 124.5, 118.7, 112.6, 111.7, 53.1, 48.2; MS (GC, m/z) 324 (M$,^+$, 100); IR (neat, cm$^{-1}$) 2953, 2924, 2852, 1734, 1454, 1433, 1333, 1303, 1268, 1219, 1193, 1163, 1106, 1078, 1022; HRMS Calcd for C$_{19}$H$_{16}$O$_5$ (M$,^+$): 324.0998; Found:
(2) Dimethyl 2-(5-(4-methoxyphenyl)benzofuran-3-yl)malonate 5fb

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{Cl} & \quad \text{O} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
2f & \quad (2.0 \text{ equiv.})
\end{align*}
\]

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{Cl} & \quad \text{O} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
5fb & \quad (91 \%)
\end{align*}
\]

The reaction of K\textsubscript{3}PO\textsubscript{4} (63.0 mg, 0.30 mmol), Pd(OAc) (1.1 mg, 0.0049 mmol), LB-phos HBF\textsubscript{4} (4.2 mg, 0.0093 mmol), 4-methoxyphenylboronic acid (45.2 mg, 0.30 mmol), 2f (41.9 mg, 0.15 mmol), 8.1 \mu L of water (8.1 mg, 0.45 mmol), and 2.0 mL of dioxane afforded 5fb (47.9 mg, 91\%) (eluent: petroleum ether/ethyl acetate = 8/1): Solid; mp 96-97 °C (petroleum ether/diethyl ether); \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \delta 7.86 (s, 1 H), 7.76-7.73 (m, 1 H), 7.58-7.48 (m, 4 H), 7.03-6.97 (m, 2 H), 4.91 (d, J = 0.3 Hz, 1 H), 3.86 (s, 3 H), 3.80 (s, 6 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz) \delta 167.8, 158.9, 154.4, 144.6, 136.4, 134.0, 128.5, 127.0, 124.2, 118.1, 114.1, 112.6, 111.7, 55.3, 53.1, 48.2; MS (GC, m/z) 354 (M\textsuperscript{+}, 100); IR (neat, cm\textsuperscript{-1}) 2957, 2924, 2852, 1734, 1518, 1465, 1435, 1335, 1304, 1268, 1218, 1163, 1106, 1078, 1021; Elemental analysis Calcd for C\textsubscript{20}H\textsubscript{18}O\textsubscript{6}: C: 67.79, H: 5.12; Found: C: 67.91, H: 5.36.

(3) Dimethyl 2-(5-(naphthalen-2-yl)benzofuran-3-yl)malonate 5fc

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{Cl} & \quad \text{O} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
2f & \quad (2.0 \text{ equiv.})
\end{align*}
\]

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{Cl} & \quad \text{O} \\
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
5fc & \quad (75 \%)
\end{align*}
\]

The reaction of K\textsubscript{3}PO\textsubscript{4} (85.2 mg, 0.40 mmol), Pd(OAc) (1.4 mg, 0.0062 mmol), LB-phos HBF\textsubscript{4} (5.5 mg, 0.012 mmol), naphthalen-2-ylboronic acid (61.0 mg, 0.40 mmol),
2f (56.4 mg, 0.20 mmol), 11.0 μL of water (11.0 mg, 0.61 mmol), and 2.0 mL of dioxane afforded 5fc (56.0 mg, 75%) (eluent: petroleum/ethyl acetate = 9/1): Solid; mp 85-86 °C (petroleum ether/dichloromethane); 1H NMR (300 MHz, CDCl3) δ 8.08 (d, J = 1.2 Hz, 1 H), 7.99-7.85 (m, 5 H), 7.80 (dd, J = 8.6 Hz, 2.0 Hz, 1 H), 7.70 (dd, J = 8.4 Hz, 1.8 Hz, 1 H), 7.61 (d, J = 8.7 Hz, 1 H), 7.58-7.47 (m, 2 H), 4.97 (s, 1 H), 3.83 (s, 6 H); 13C NMR (CDCl3, 75 MHz) δ 167.8, 154.8, 144.7, 138.8, 136.6, 133.6, 132.4, 128.3, 128.1, 127.6, 127.1, 126.3, 126.02, 125.95, 125.8, 124.7, 118.9, 112.7, 111.8, 53.1, 48.2; MS (GC, m/z) 374 (M+, 100); IR (neat, cm^-1) 2954, 2924, 2852, 1751, 1734, 1454, 1434, 1331, 1303, 1269, 1194, 1154, 1105, 1076, 1021; Elemental analysis Calcd for C23H18O5: C: 73.79, H: 4.85; Found: C: 73.86, H: 4.93.

(4) Methyl 2-phenyl-2-(6-phenylbenzofuran-3-yl)acetate 5ia

The reaction of K3PO4 (148.7 mg, 0.70 mmol), Pd(OAc)2 (1.4 mg, 0.0062 mmol), LB-phos/HBF4 (5.6 mg, 0.012 mmol), phenylboronic acid (49.1 mg, 0.40 mmol), 2i (60.3 mg, 0.20 mmol), 11.0 μL of water (11.0 mg, 0.61 mmol), and 1.0 mL of dioxane afforded 5ia (59.4 mg, 86%, eluent: petroleum/ethyl acetate = 20/1): Solid; mp 119-120 °C (petroleum ether/dichloromethane); 1H NMR (300 MHz, CDCl3) δ 7.74 (dd, J = 8.7 Hz, 0.9 Hz, 2 H), 7.66-7.60 (m, 2 H), 7.51-7.29 (m, 10 H), 5.18 (s, 1 H), 3.80 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 172.1, 155.9, 143.7, 141.1, 138.3, 136.8, 128.8, 128.3, 127.8, 127.3, 127.2, 126.1, 122.3, 120.0, 118.0, 110.1, 52.5, 47.8; MS (GC, m/z) 342 (M+, 45.26), 283 (100); IR (neat, cm^-1) 2956, 2923, 2853, 1730, 1566, 1497, 1473, 1454, 1433,
1306, 1272, 1253, 1226, 1194, 1157, 1093, 1079, 1066, 1007; Elemental analysis Calcd for C_{23}H_{18}O_{3}: C: 80.68, H: 5.30; Found: C: 80.39, H: 5.33.

(5) Methyl 2-(6-(4-methoxyphenyl)benzofuran-3-yl)-2-phenylacetate 5ib

\[
\text{Ph} \quad \text{CO}_2\text{Me} \\
\text{Cl} \quad \text{B(OH)}_2
\]

\[
\begin{align*}
\text{Ph} \quad \text{CO}_2\text{Me} \\
\text{OMe} \quad \text{Cl}
\end{align*}
\]

The reaction of K_{3}PO_{4} (74.7 mg, 0.35 mmol), Pd(OAc) (0.8 mg, 0.0036 mmol), LB-phos·HBF_{4} (3.0 mg, 0.0066 mmol), 4-methoxyphenylboronic acid (30.7 mg, 0.20 mmol), 2i (32.4 mg, 0.11 mmol), 5.4 μL of water (5.4 mg, 0.30 mmol), and 1.0 mL of dioxane afforded 5ib (34.9 mg, 87%) (eluent: petroleum ether/ethyl acetate = 15/1): Solid; mp 137-138 °C (petroleum ether/diethyl ether); \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.69 (d, \(J = 1.2\) Hz, 1 H), 7.65-7.62 (m, 1 H), 7.57-7.50 (m, 2 H), 7.46-7.41 (m, 2 H), 7.40-7.29 (m, 5 H), 7.02-6.95 (m, 2 H), 5.14 (s, 1 H), 3.85 (s, 3 H), 3.78 (s, 3 H); \(^{13}\)C NMR (CDCl\textsubscript{3}, 75 MHz) \(\delta\) 172.2, 159.1, 156.0, 143.5, 138.0, 136.9, 133.7, 128.8, 128.4, 128.3, 127.8, 125.6, 122.0, 119.9, 118.0, 114.2, 109.6, 55.3, 52.5, 47.9; MS (GC, m/z) 372 (M\(^+\), 75.48), 313 (100); IR (neat, cm\(^{-1}\)) 2958, 2834, 1734, 1605, 1519, 1479, 1455, 1436, 1362, 1300, 1278, 1239, 1181, 1155, 1138, 1108, 1093, 1075, 1036, 1020; Elemental analysis Calcd for C_{24}H_{20}O_{4}: C: 77.40, H: 5.41; Found: C: 77.57, H: 5.29.

(6) Methyl 2-(6-(naphth-2-yl)benzofuran-3-yl)-2-phenylacetate 5ic
The reaction of K$_3$PO$_4$ (111.7 mg, 0.53 mmol), Pd(OAc)$_2$ (1.1 mg, 0.0049 mmol), LB-phosHBF$_4$ (4.1 mg, 0.0091 mmol), naphth-2-ylboronic acid (51.2 mg, 0.30 mmol), 2i (45.3 mg, 0.15 mmol), 8.1 µL of water (8.1 mg, 0.45 mmol), and 2.0 mL of dioxane afforded 5ic (50.0 mg, 84%) (eluent: petroleum ether/ethyl acetate = 50 /1): Solid; mp 142-143 °C (petroleum ether/diethyl ether); $^1$H NMR (300 MHz, CDCl$_3$) δ 8.10-8.06 (m, 1 H), 7.96-7.84 (m, 4 H), 7.81-7.76 (m, 2 H), 7.60-7.31 (m, 9 H), 5.20 (s, 1 H), 3.82 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 172.1, 156.0, 143.8, 138.4, 138.1, 136.8, 133.6, 132.5, 128.8, 128.43, 128.35, 128.1, 127.8, 127.6, 126.3, 126.2, 125.9, 125.7, 122.5, 120.1, 118.0, 110.3, 52.5, 47.8; MS (GC, m/z) 392 (M$^+$, 60.18), 333 (100); IR (neat, cm$^{-1}$) 2955, 2921, 1730, 1494, 1434, 1374, 1309, 1252, 1224, 1150, 1129, 1097, 1079, 1065, 1009; Elemental analysis Calcd for C$_{27}$H$_{20}$O$_3$: C: 82.63, H: 5.14; Found: C: 82.48, H: 5.26.

References


$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra